

Electronic Supplementary Information

A facile approach to fabricate halloysite/metal nanocomposites with preformed and *in-situ* synthesized metal nanoparticles: A comparative study of their enhanced catalytic activity

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Materials

All chemicals were used as received. Halloysite nanotubes (HNTs), gold(III) chloride trihydrate ($\geq 99.9\%$), silver nitrate (99.9999%), 1-octadecene, oleylamine (70%), and sodium borohydride (NaBH_4) were purchased from Sigma-Aldrich. (3-aminopropyl) triethoxysilane (APTES, 97%) and 2-nitrobenzoic acid were received from Alfa Aesar. Toluene was obtained from Merck. 4-nitrobenzoic acid, 2-nitrophenol, and 4-nitrophenol (4-NP) were received from Sisco Research Laboratory, India.

Characterization

Fourier transform infrared (FTIR) spectra were recorded in the range of 400 to 4000 cm^{-1} using JASCO FT/IR 6300. Powder X-ray diffraction (XRD) analysis was carried out by RIGAKU MiniFlex II powder diffractometer using $\text{Cu K}\alpha$ radiation with 35 kV beam voltage and 15 mA beam current. The morphology of HNTs was characterized using transmission electron microscopy (TEM: FEI TECNAI G2 F20-ST) operating at 200 kV and field emission scanning electron microscopy (FESEM: FEI QUANTA FEG 250) after drop casting a drop of solution on a carbon coated copper grid and silicon wafer respectively. High resolution transmission electron microscopy (HR-TEM) and Energy dispersive X-ray spectroscopy (EDX) have been performed in the above mentioned TEM operating at 200 kV. UV-visible absorption spectra were recorded at room temperature using a Shimadzu spectrometer, UV-2600.

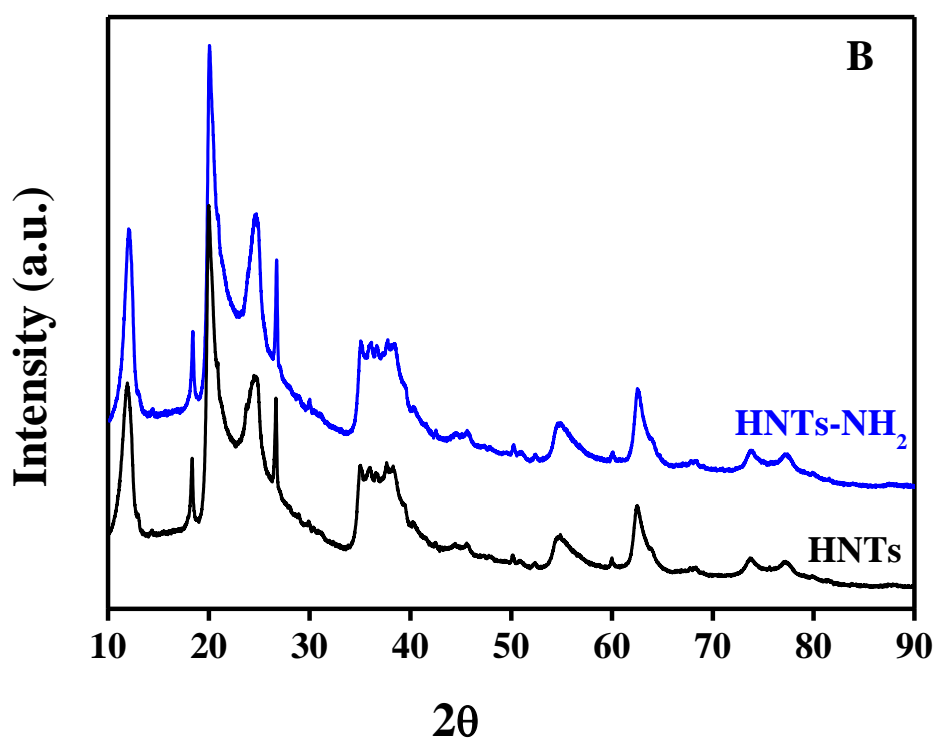
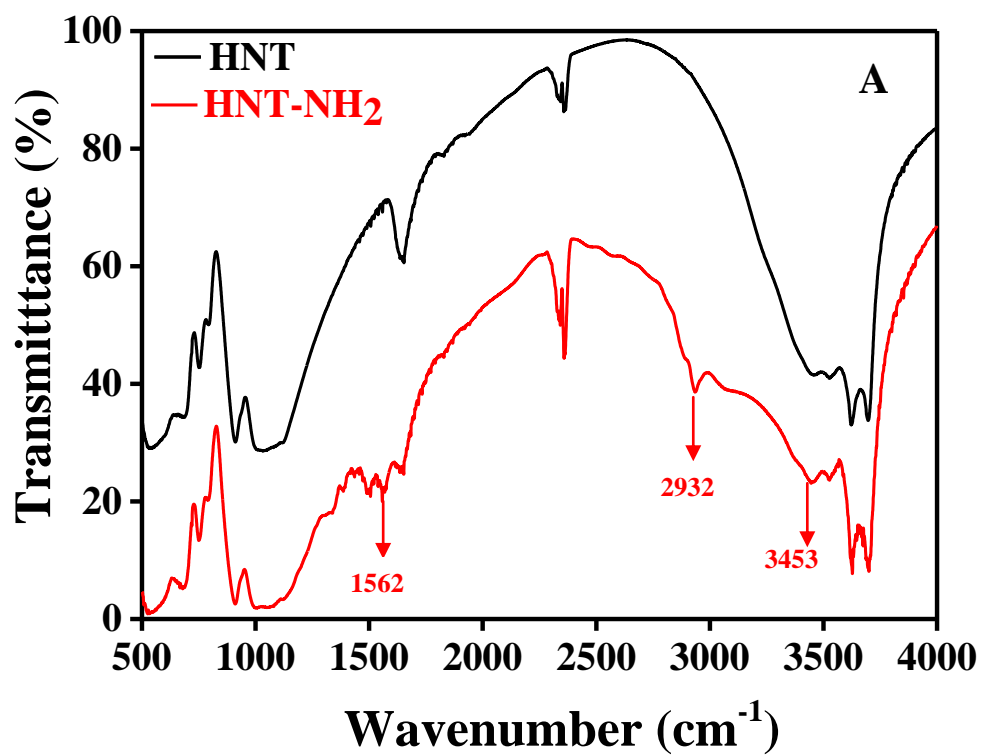


Fig. S1 (A) FTIR spectra and (B) XRD patterns of HNTs and aminosilane modified HNTs (HNTs-NH₂) respectively.

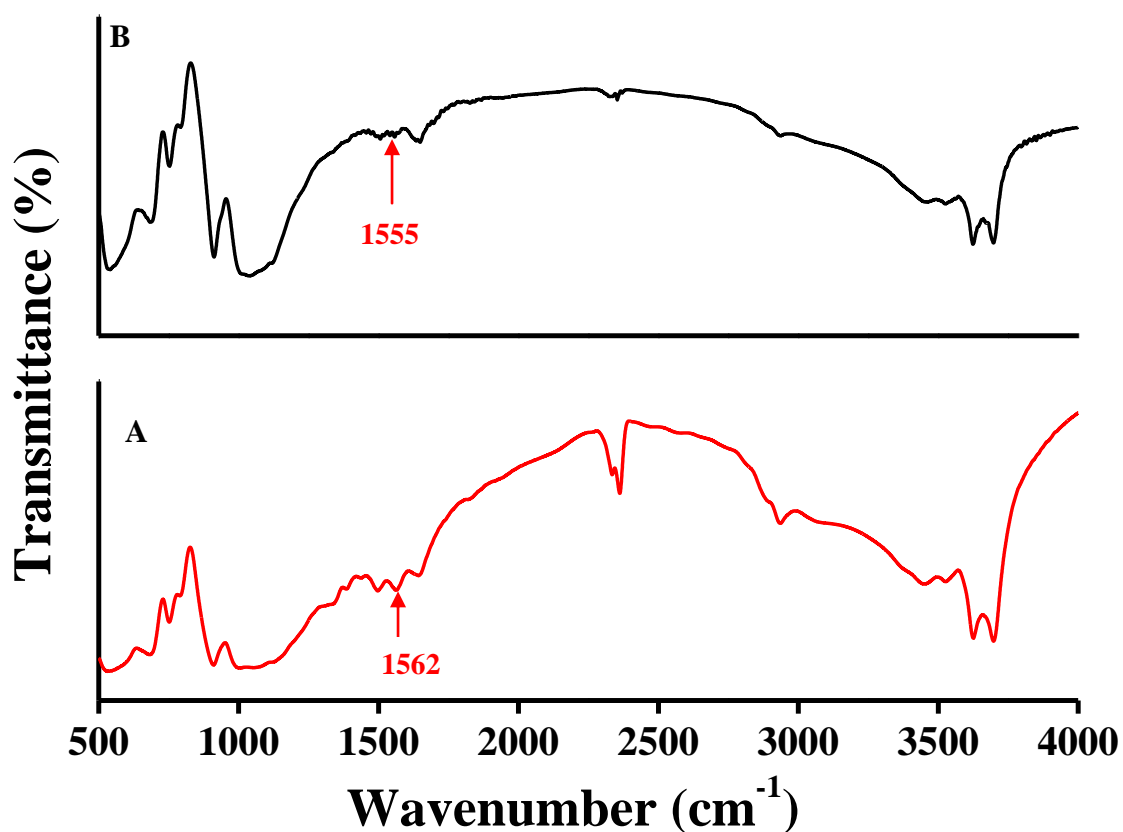


Fig. S2 Representative FTIR spectra of (A) HNTs-NH₂ and (B) HNTs/Ag nanocomposites, synthesized after immobilization of Ag NPs over the surface of HNTs-NH₂. FTIR analysis further demonstrates the immobilization of metal NPs over the surface of HNTs-NH₂. After the immobilization of Ag NPs, the intensity of the peak at 1562 cm⁻¹ for N-H deformation in HNTs-NH₂ has been decreased and shifted to 1555 cm⁻¹, which further demonstrated that the aminosilane behaves as a linker molecule and strengthen the interfacial adhesion of NPs over HNTs surfaces.

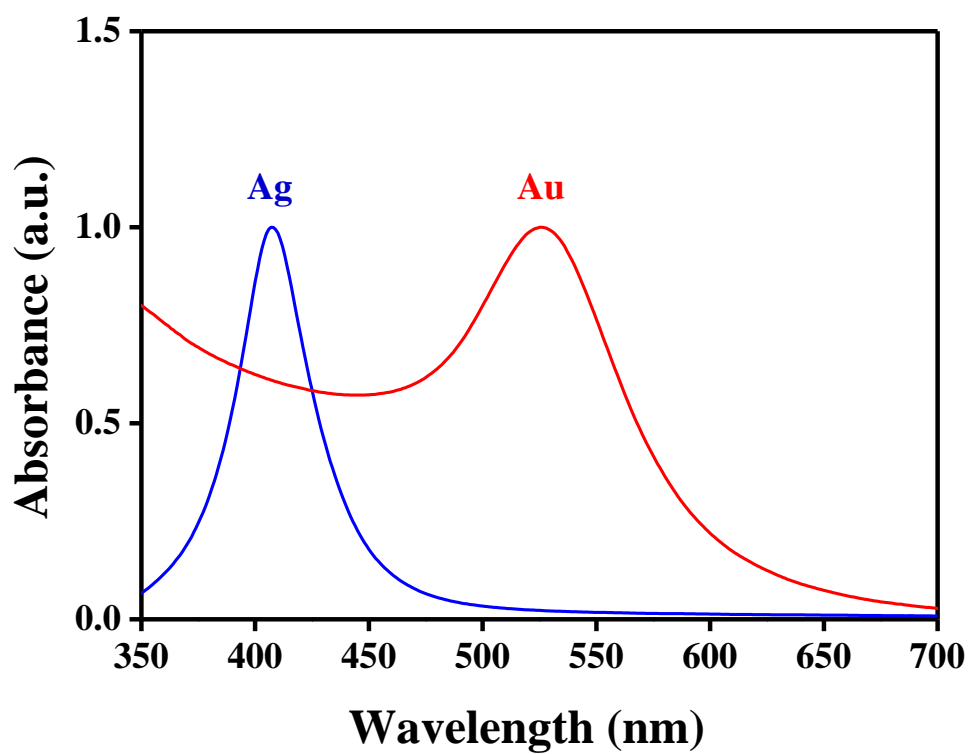


Fig. S3 UV-Visible absorption spectra of colloidal Au and Ag nanoparticles before immobilization over the surface of aminosilane modified HNTs (HNTs-NH₂).

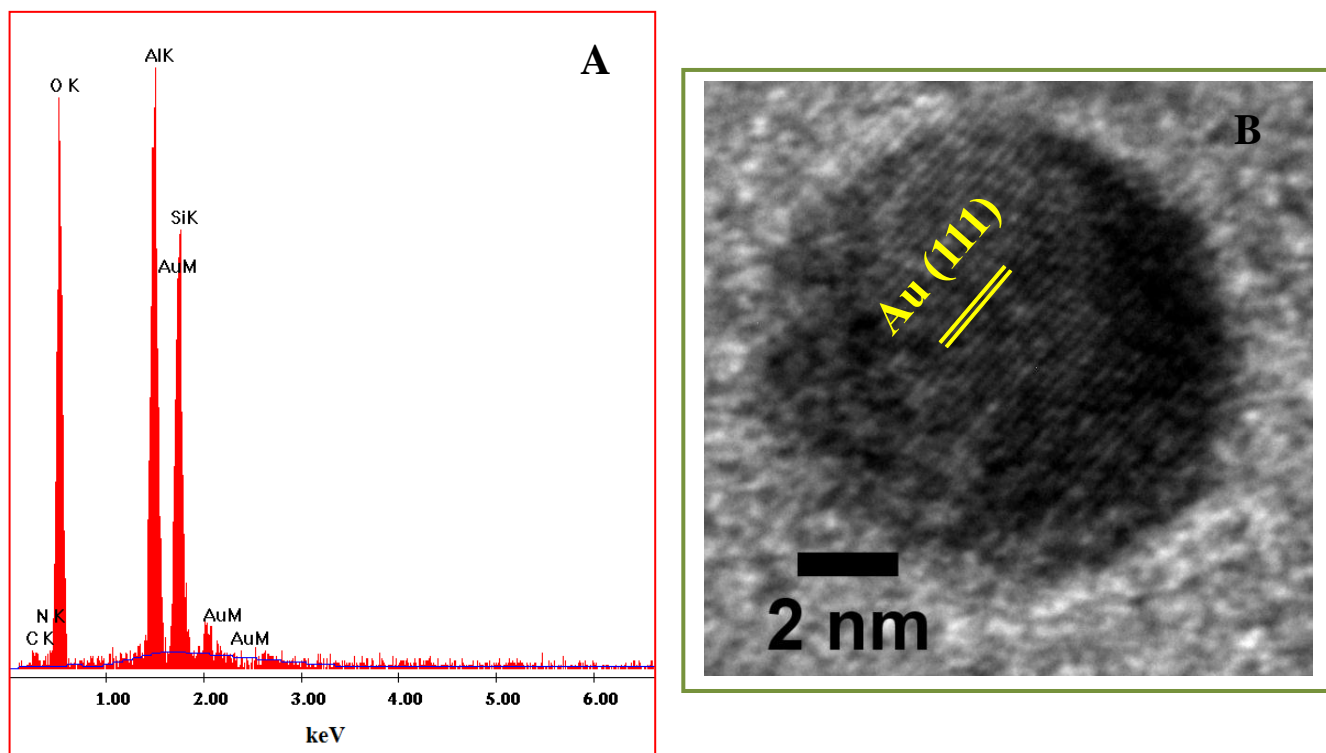


Fig. S4 (A) A representative EDX spectrum of preformed HNTs/Au nanocomposites, indicating the presence of Au nanoparticle in the nanocomposites. (B) HRTEM image of Au nanoparticles loaded over the surface of aminosilane modified HNTs, demonstrating (111) planes of the fcc Au.

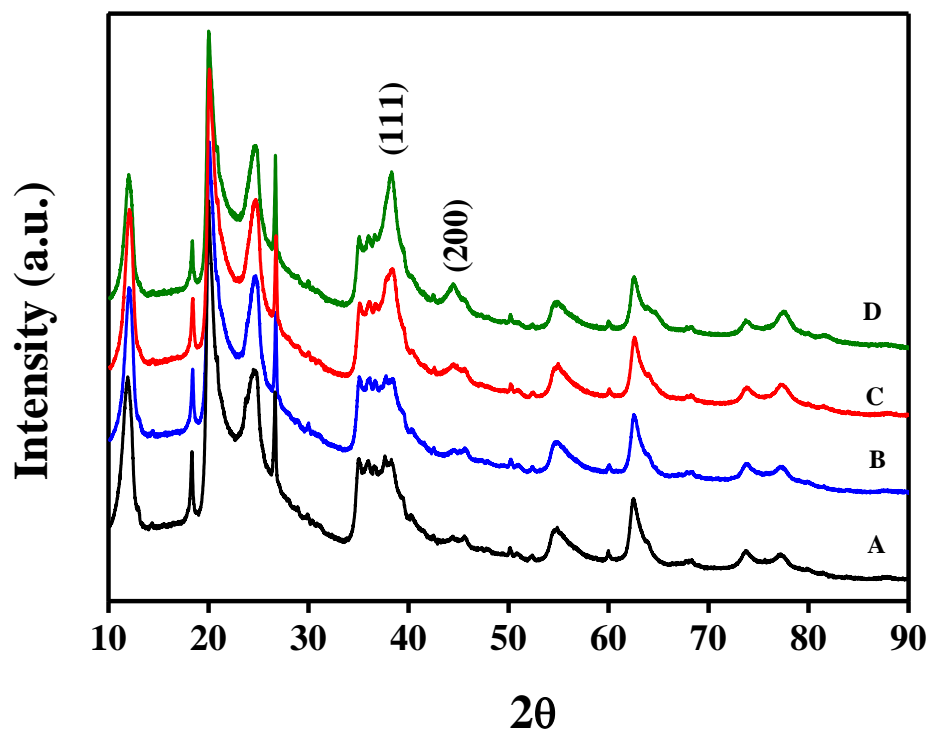


Fig. S5 XRD patterns of (A) HNTs and (B) aminosilane modified HNTs (HNTs-NH₂). (C) and (D) XRD patterns of *in-situ* synthesized HNTs/Ag and HNTs/Au nanocomposites respectively, demonstrating the formation HNTs/metal nanocomposites through the immobilization of their respective precursor followed by the reduction using sodium borohydride.

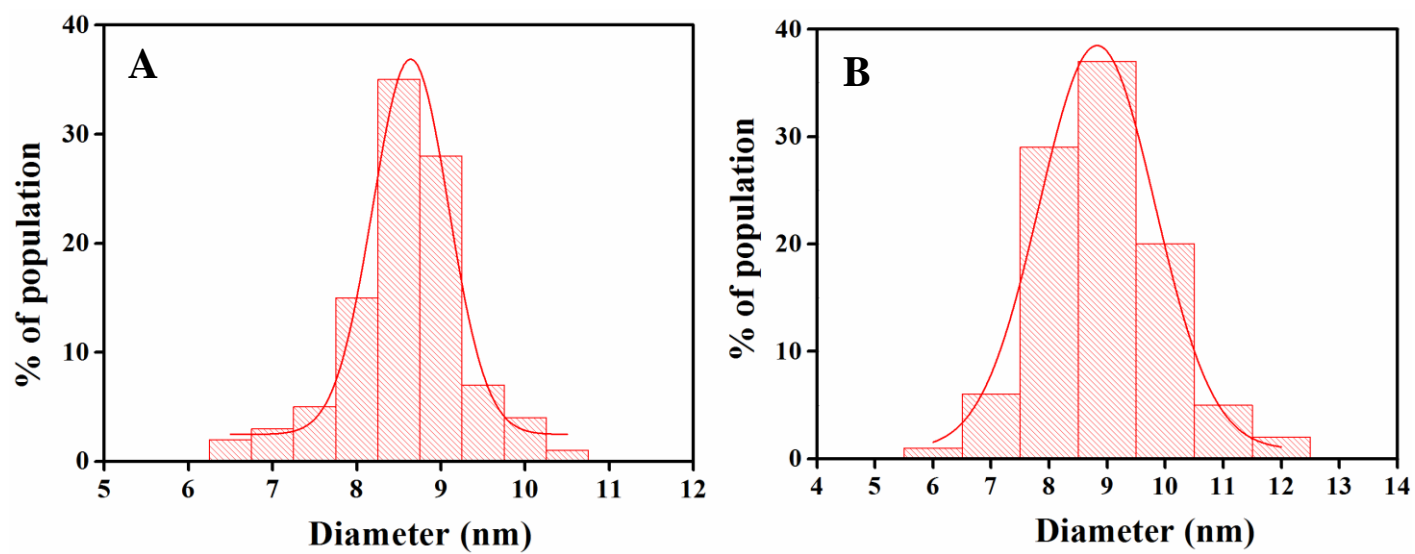


Fig. S6 Histograms of particle size distribution of Ag nanoparticles immobilized in (A) preformed and (B) *in-situ* synthesized HNTs/Ag nanocomposites.

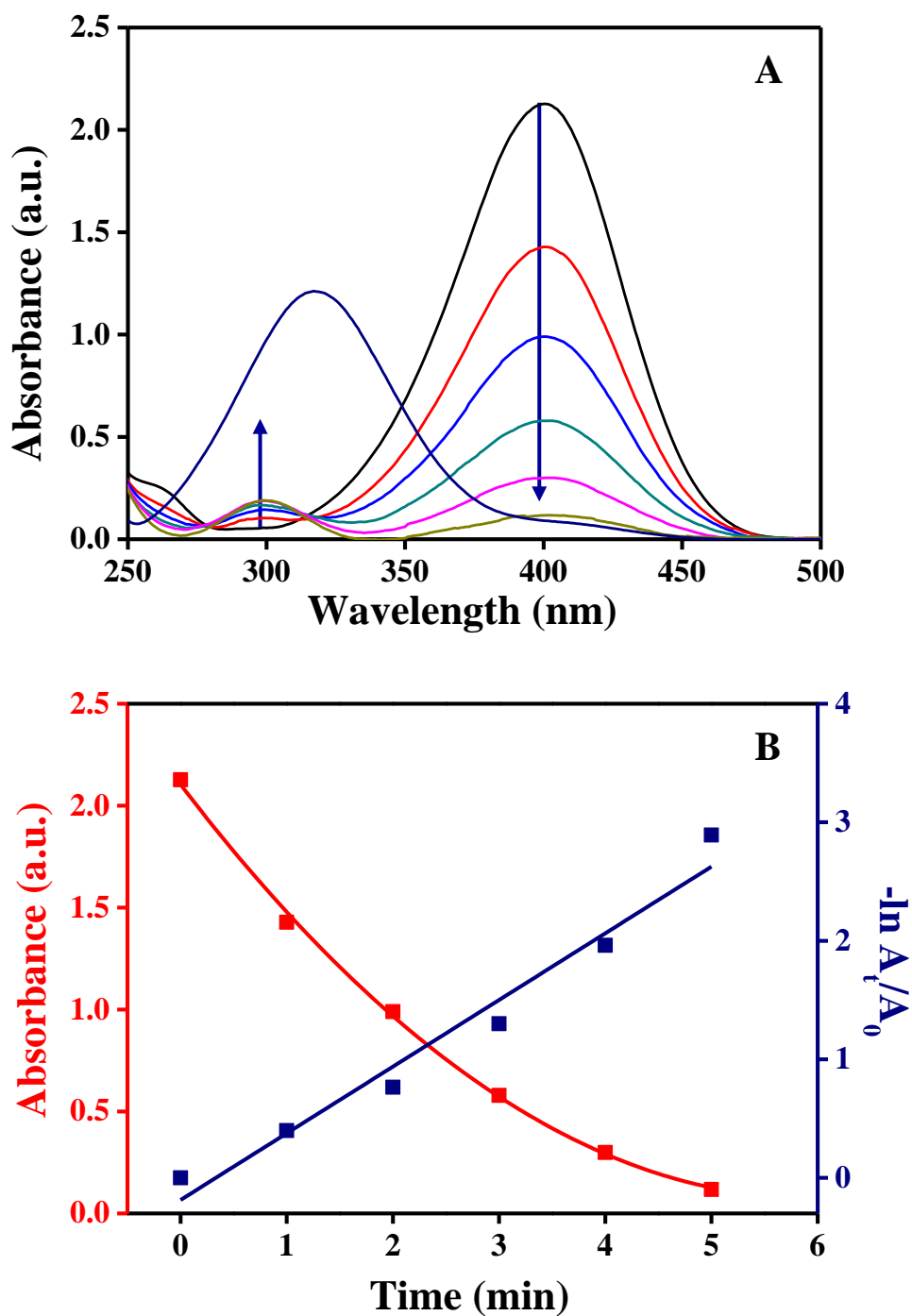


Fig. S7 (A) UV–Visible spectra for the successive reduction of 0.1 mM 4-NP using 0.1 M NaBH₄, in presence of 2.0 mg of preformed HNTs/Ag nanocomposites at an interval of 1 min. (B) plot of absorbance and $\ln A_t/A_0$ as a function of reaction time for pseudo-first-order reduction kinetics of 4-nitrophenol.